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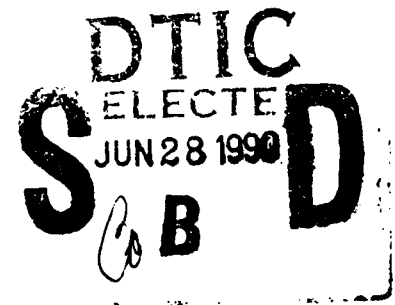
TECHNICAL REPORT NO. 10

Modification of Polystyrene/Polybutadiene Block Copolymer Films
by Chemical Reaction with Bromine and Effect on Gas Permeability

by

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MODIFICATION OF POLYSTYRENE/POLYBUTADIENE BLOCK
COPOLYMER FILMS BY CHEMICAL REACTION WITH BROMINE
AND EFFECT ON GAS PERMEABILITY

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Abstract

Permeability coefficients (P) for several gases were measured in heterogeneous polystyrene/polybutadiene (PS/PB) block copolymer films before and after reaction with aqueous bromine. Films reacted to low and very high extents exhibited decreases in P and increases in selectivity compared to the starting material. At intermediate reaction extents, effective permeability coefficients in the reacted materials were higher than those in the unmodified films, resulting in membranes which exhibited both selectivity and permeability enhancement relative to the starting PS/PB system. These effects on permeability are the combined result of physical and chemical changes in the block copolymer films caused by the bromination reaction.



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Introduction

The gas transport properties of polymeric materials¹ can be altered by chemical modification^{2,3,4}. Often, the goal of these modifications is to create either a material with enhanced barrier capabilities, or one which exhibits a combination of high permeability and selectivity. These criteria reflect the two most prominent applications for polymers in which gas transport is crucial--packaging materials and membranes for gas separations^{5,6,7}.

Systematic chemical modifications of polymers such as polyimides⁴ and silicones³ have demonstrated that judicious incorporation of particular segments or groups into a polymer chain can affect the material's gas permeability coefficient (P) through changes in either the diffusion coefficient (D) or the solubility coefficient (S). The addition of bulky segments into the polymer can result in either a decrease in D as a result of restricted chain mobility, or an increase in D due to reduced segmental density. S on the other hand, can be adjusted by modifying the polymer so that it contains chemical groups which present a particular thermodynamic interaction with the penetrant.

Most of the work on transport in chemically modified polymers has been conducted using homopolymers. Here, we examine gas transport in microphase separated polystyrene/polybutadiene (PS/PB) block copolymer films that have been reacted with bromine, which is expected to add

readily to the unsaturated sites of the rubbery PB--the high permeability rubber component of the block copolymer⁸.

Effects on the diffusion and permeability coefficients in the reacted material may be expected because of bromine's large atomic size. In addition, the incorporation of the massive Br atoms may induce microstructural changes in the solid block copolymer. Of particular interest is whether the chemical modification of the block copolymer leads to markedly different effects on gas permeability than those observed in the corresponding modified homopolymers, and whether any changes offer improved characteristics for gas separations or barrier applications.

Experimental

The block copolymer used in this study was supplied by Phillips Petroleum Co., and has been used previously in studies relating gas permeability to block copolymer morphology^{8,9,10}. This material contains 75 vol% PS and has a weight average molecular weight of 180,000 g/mol. Additional molecular characterization information can be found elsewhere⁸.

Sample films were prepared from an extruded sheet of the K-Resin, 0.5 mm in thickness. These samples are referred to as KR-E, for "K-Resin: extruded". Figure 1 is a transmission electron micrograph (TEM) of an osmium-stained thin section which presents a cross sectional view of a KR-E specimen parallel to the extrusion direction. As indicated

in the Figure, a gas molecule permeating through these samples will travel through a random, alternating PB/PS lamellar microstructure with a PB lamellar thickness of ca. 75 Å. More detailed morphological characterization of this material has been described in an earlier publication⁸.

Polybutadiene and polystyrene homopolymers, both of nominal molecular weight 200,000, were obtained from Polysciences, Inc., and Scientific Polymer Products, Inc., respectively. Homopolymer films were cast on a flat Teflon surface from solution in toluene. PB films were mildly crosslinked by exposure to a 5 Mrad dose of electron beam radiation¹¹.

Reaction was conducted by submerging the polymer films in a 0.1 M solution of bromine in distilled water. (There is some precedent to the reaction of solid polymers with bromine in this manner--aqueous solutions of bromine were used as an early electron microscopy stain for diene polymers¹².) Films were hung vertically from a Teflon support in a closed glass jar which contained the solution. After remaining in the container for a given amount of time, the test films were rinsed in distilled water for 24 hr, then exposed to vacuum for four days.

PB and PS homopolymer films were also subjected to the aqueous bromine treatment. As anticipated, PB films experienced a weight gain after reaction, and took on an orange color which increased in intensity with greater reaction time. Based on published accounts of halogen

reaction with diene polymers and low molecular weight alkenes^{13,14}, there are several mechanisms of varying complexity which may describe the reaction of aqueous bromine with PB. In general however, it can be expected that the reaction will result in either the addition of two Br atoms to the carbon-carbon double bond, or the incorporation of a single Br atom to a double bond with the formation of a crosslink between adjacent chains.

The reacted PB films became noticeably less flexible as reaction time increased, and a sample reacted for 18.5 hours exhibited a glass transition in differential thermal calorimetry at 35 °C (unreacted PB T_g = -80 °C). This result indicates substantial reduction of chain mobility in the PB (a consequence of the addition of the bulky bromine atoms to the chains) along with possibly increased crosslink density.

Solid polystyrene films also exhibited a detectable increase in weight after reaction with bromine. Solution C^{13} NMR of the brominated product indicated the presence of Br on the phenyl group, likely at the para position. There was no evidence of bromine on the polymer backbone.

A series of reactions using square 3 x 3 inch KR-E block copolymer films was conducted. Extent of reaction was characterized by the percentage change in weight of the samples (hereafter referred to as %W). Figure 2 is a plot of %W versus reaction time in hours. The curvature concave to the time axis suggests a reaction process whose rate is

controlled by diffusion of the reactant into the polymer film. Sample weight gains as large as 73% (after reaction for 95 hr) were achieved. The maximum possible weight increase of the block copolymer, based on addition of two Br atoms to every PB double bond (an upper limit because of the crosslinking possibility) and one to every PS phenyl group, is 108%.

Changes in the thickness of reacted block copolymer films were observed. Sample thicknesses as a function of %W appear in Figure 3. There is a steady increase in thickness with reaction extent, which levels at a value of 0.605 mm at %W = 44. Beyond this point, considerable weight increases are detected with reaction without further significant changes in sample thickness.

Several visual observations of the originally transparent KR-E films indicated that both physical and chemical changes had occurred in the reacted material. Up to 8 %W, the block copolymer films remained transparent, but took on an orange color similar to that observed in the reacted PB films. After 8 %W, increasing cloudiness was observed to 35 %W, beyond which the samples were completely opaque and red-gray in color. This opacity is a possible indication of the presence of crazes or other heterogeneities in the sample which are somewhat larger than the original 75 Å microdomain size (which does not cause appreciable scattering of visible light).

A cross-sectional view of a sample which had become visibly opaque revealed that the gray color was present only near the film surface, while the interior regions retained the orange color that was observed in the earlier stages of the reaction. This formation of a "skin layer", with a core visibly changed from the starting material, indicates the possibility of two distinct events during the reaction process--one which results in the orange coloration, the second which causes the material to become opaque. A more detailed examination of sample cross-sections using scanning electron microscopy (SEM) is presented in the following section.

Results and Discussion

Gas permeability coefficients in KR-E reacted to various extents were measured at 25 °C for several gases using a variable volume permeability apparatus¹⁵. P_s for unreacted PB, PS, and KR-E films appear in Table I. These permeability coefficients for materials which have not been chemically modified will be referred to as P_0 .

Relative permeabilities, defined as P divided by P_0 , for the bromine-reacted block copolymer films as a function of reaction extent to 15 %W appear in Figure 4. Permeability coefficients are seen to decrease with extent of reaction. Note that all gases are not affected to the same degree--permeation of the larger penetrants is retarded significantly, while the transport rate of the relatively

small species He is virtually unchanged from that in the starting material. The addition of the bulky halogen and resulting decrease in chain mobility clearly causes the reacted material to selectively inhibit gas transport on the basis of size.

The result of this enhanced screening ability after reaction is a change in the selectivity or separation factor (defined as the ratio of P_s for two gases) for any gas pair considered. The largest change in selectivity is for the He-CH₄ pair, which is increased by a factor of four. The fact that this is achieved with no appreciable decrease in He permeability is especially interesting from a membrane separations standpoint.

As opposed to a simple monotonic decrease in block copolymer permeability with extent of bromination, unexpected changes in permeation behavior were observed at reaction extents higher than 15 %W. Permeability coefficients for all gases increased to a maximum near 45 %W, followed by a subsequent decrease (Figure 5). (P/P_0) values at some reaction extents exceed 1, indicating greater permeation rates than those in the original KR-E samples. Despite this unusual variation in permeability coefficients, further significant changes in separation factors (beyond those achieved at 15 %W) are not seen--the percentage change in permeation rates for each gas is similar throughout the reaction range beyond 15 %W.

Returning to the He-CH₄ gas pair, the behavior of the brominated KR-E at 44 %W (where it exhibits the highest He permeability) represents an appealing property change from the starting material. It exhibits a increase in selectivity for the He-CH₄ separation by a factor of approximately four, as well as a nearly six-fold increase in He permeability. This combined improvement in selectivity and permeability is unusual, and certainly desirable from a gas separations standpoint.

To gauge the significance of the property changes in the 44 %W material, consider the separation factor vs. permeability plot of Figure 6. In the Figure, the He-CH₄ separation factor is plotted against the He permeability coefficient for a variety of polymers. Data to construct the filled squares of the plot were taken from several sources^{16,17,18}. The nature of this plot is typical for many gas pairs. All of the polymers fall in a negatively sloping narrow band, demonstrating the commonly observed tradeoff between selectivity and permeability in polymeric materials. Because in membrane separations both high permeability and high selectivity are desired, a superior polymer for the separation would appear to the upper right of this band in the Figure.

The open squares of the plot are experimentally determined points for the original KR-E material, and KR-E after bromination to 44 %W. Note that the original PS/PB block copolymer lies within the zone established by the

other polymers. After reaction to 44 %W, the increase in P and in the ideal separation factor cause the KR-E point to be shifted well outside the range of typical behavior. Within the framework of the many polymers considered, the change in transport properties exhibited by the brominated K-Resin does in fact represent a significant improvement and departure from the norm.

To more thoroughly characterize the permeability behavior the block copolymer throughout the entire reaction range, permeability coefficients for CO₂ alone were obtained in additional samples. The resulting plot of p^{CO_2} vs. %W appears in Figure 7. This unmistakably shows the decrease, increase and subsequent decline of permeability throughout the reaction range, and identifies a permeability minimum and maximum at 25 and 48 %W, respectively.

Note that Figures 5 and 7 have been divided into regions I, II, and III. While the permeability decrease and selectivity enhancement of region I can be attributed to a lowering of polymer segmental mobility caused by addition of large Br atoms, the behavior in regions II and III is more difficult to interpret. The increase in P of region II is indicative of an opening or expansion of the polymer structure, which is also suggested by the increase in sample thickness up to 44 %W (Figure 3). This "opening" is then halted or reversed in region III. Note that the onset of region III corresponds to the reaction extent beyond which sample weight increases were detected without further

increases in sample volume (as indicated by thickness measurements--Figure 3).

In order to gain insight into structural changes occurring in the reacted block copolymer, film cross sections were examined using SEM. Before being gold plated for SEM viewing, samples were embedded in epoxy, and a fresh surface was cut and polished using a 0.05 μm polishing compound. The samples were cut in such a way so as to view the cross section of the sample film from same direction as the view presented in the TEM of Figure 1.

Micrographs at various reaction extents appear in Figure 8. As reaction proceeds from 0 to 25 %W, a discernable layer or front, indicated by a light coloration in the micrograph, is seen to grow from the film surfaces toward the center. At 35 and 48 %W, the steady growth of this surface layer has been replaced by a more rapid development of the light colored regions, which have extended toward the film center in thin, finger-like regions. Recall that it is at these reaction extents where the sudden increase in permeation rates were observed (Figs 5,7). The fact that these growing regions appear light in color indicates that they either have a markedly different bromine concentration than the remainder of the film¹⁹, or that they are porous in nature (increased electron emission would occur at the "edges" of small pores). Beyond %W of 48, no further development of the light colored regions was apparent. This extent of reaction corresponds to the point

beyond which permeability coefficients ceased to increase, and no increases in sample thickness with further reaction time were observed. This leads to the conclusion that the material appearing white in the SEM may be a low density, microporous material which is highly permeable to gases. The fact that an intact portion of the brominated samples near their center remains unaffected (dark in SEM) would be consistent with the observation that the separating quality of these films is maintained, even though the outer portions of their cross sections may now allow rapid, nonselective gas transport.

Direct evidence that the growing surface layer observed in these micrographs is more permeable to gases than the core is presented by a study of non-steady state gas sorption. If the reacted block copolymer films contain a high permeability outer layer, the rate of transient gas uptake in a standard sorption experiment should deviate in a predictable manner from that expected for a homogeneous sample.

Information from a sorption experiment is commonly presented as a plot of M_t/M_∞ (mass of gas uptake divided by uptake at equilibrium) vs. $\text{time}^{1/2}$. For homogeneous polymers with a constant gas diffusion coefficient, such a plot is linear to M_t/M_∞ values of 0.6 or higher, after which it displays curvature concave to the $\text{time}^{1/2}$ axis²⁰. The slope of the linear region is proportional to the gas diffusion coefficient.

In order to investigate what qualities are to be expected in a sorption curve for a film containing a high diffusivity surface layer, a computer simulation of the sorption process was conducted. Using the finite difference numerical method, the simulation considers transient gas uptake by a two component (A and B) polymer laminate which is discretized into many elements. The model considers a film composed of three layers--ABA. Each component is assigned a constant gas diffusion coefficient, with D higher in surface material (A) than in the core (B). The gas solubility in each layer is considered to be identical.

Figure 9 is a simulated sorption curve for a laminate in which $D_A/D_B = 10$, and the overall amounts of the surface and core material are equivalent. The plot deviates from the initial linearity at an M_t/M_∞ value much less than 0.6. This is followed by a second nearly linear region of lower slope, and finally by asymptotic curvature to $M_t/M_\infty = 1$.

An experimental CO_2 sorption study was conducted on the KR-E sample brominated to 25 %W (refer to the SEM for this sample in Figure 8) to compare with the numerical simulation. Gas uptake into the initially evacuated sample was measured by monitoring the pressure decay in a closed sample chamber during sorption. Details of the experimental setup are described elsewhere²¹. Figure 10 contains a sorption curve at an applied CO_2 pressure of 1 atm. The shape of the curve does not conform to the standard sorption curve expected for homopolymers. Instead, it exhibits the

features seen in the sorption simulation into the laminate, and is therefore consistent with expectations for diffusion into a film whose outer regions exhibit higher permeability than its interior. Based on these observations, we conclude that the light colored regions observed in the SEM are in fact microporous and highly permeable.

Some information on the structure of the microporous material is contained in transmission electron micrographs of thin sections from the 48 %W sample (the sample which exhibited the highest CO₂ permeability). The sections were taken from the center portion of the film, where the thin, parallel extensions of light colored regions were observed in SEM. The TEM of Figure 11 clearly shows the presence of crazes in the sample. These crazes extend for very long distances (relative to their thickness) parallel to one another in a direction normal to the film surface. The distance between adjacent crazes is approximately 20 μ m. This is similar to the measured distance between the light colored parallel "fingers" in the corresponding SEM (Figure 8).

Permeability coefficients in polystyrene and polybutadiene homopolymers reacted in similar fashion behaved quite differently, and more predictably, than those in the KR-E block copolymer. PS and PB films (of similar dimensions to the KR-E samples) were exposed to the bromine solution for up to 18.5 hours. This final reaction time for the homopolymers corresponds roughly to the reaction time

for which the block copolymer exhibited its maximum CO₂ permeability.

For PB, CO₂ permeability coefficients decreased steadily by over three orders of magnitude through the highest reaction time of 18.5 hours. What had initially been a highly permeable rubber was transformed by the reaction into a material which is a reasonably good barrier to CO₂ transport. The helium permeability coefficient decreased only by 30% after the same extent of reaction. This disproportionate reduction in the permeability of the large CO₂ species is caused by the chain mobility reduction in the brominated rubber, which was documented by the calorimetry results described in the experimental section. Further studies of transport in halogenated polybutadiene, including measurement of D and S for a variety of gases, are currently underway.

The reacted PS also displayed a reduction in CO₂ permeability after reaction, although the decrease is modest in comparison to that of the PB--approximately 30% after 18.5 hours of reaction.

An important conclusion from the permeation studies of reacted homopolymers is that no increases in P are observed in either PB or PS homopolymers which were reacted under identical conditions to the KR-E samples. This effect is unique to the microphase separated block copolymer.

Conclusions

The sum of evidence presented above indicates that there are two distinct processes that occur during the reaction of KR-E block copolymer films with bromine, both of which affect its gas permeability. The first is a chemical change within the domains of the microstructure. As with PB homopolymer films, this results in decreases in chain mobility and reduced permeability. It is this mechanism which results in the increased ability to screen larger gas molecules and the enhancement of separation factors observed in the reacted block copolymer, an effect also observed in the PB samples.

The second process is an opening of the block copolymer structure, at least in part through the formation of low density craze matter. Microporous, high permeability regions, with little if any ability to distinguish between different gas molecules, grow inward from the film surface as the reaction proceeds. Their formation is likely a result of the block copolymer's attempt to accommodate the incorporation of large Br atoms into the PS and PB microdomains.

The trends observed in the permeability plots, Figures 5 and 7, can be summarized as follows. In region I, the effects of the chemical change and the growth of a microporous surface layer compete with one another. The chemical change results in an enhancement in selectivity, but KR-E permeabilities do not fall as rapidly with $\%W$ as in the PB homopolymer because rapid transport is occurring near

the film surface. In region II, the porous material and resulting high flux permeation pathways extend deep into the sample thickness. The effective thickness of the membrane is thereby greatly reduced, resulting in abrupt increases in P to above the values exhibited by the original unmodified material. In region III, the formation of porous material has slowed or ceased altogether, and further chemical reaction again lowers P .

The KR-E sample reacted to 44 %W displayed enhanced selectivity and permeability (Figure 6). This favorable and unusual behavior is the combined result of the concurrent processes described above. A large portion of the film structure for this sample was microporous--essentially a support material with little resistance to transport. The remaining chemically reacted dense regions, now effectively much thinner than the original sample thickness, were able to separate gaseous penetrants on the basis of size. In this manner, the brominated block copolymer can be considered a new type of asymmetric gas separation membrane--the product of chemically induced changes in physical as well as chemical structure.

Acknowledgements

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Captions for Figures

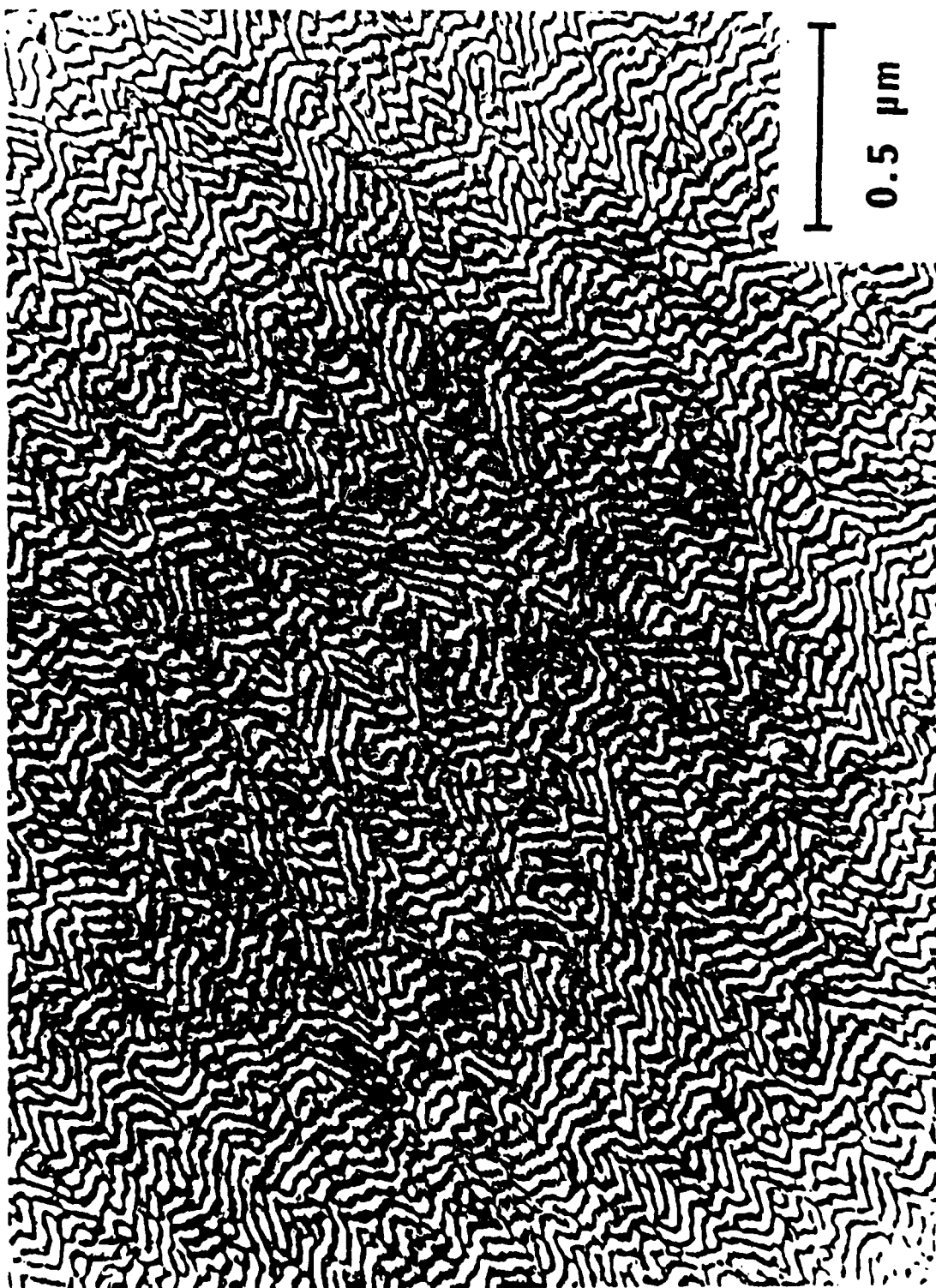
1. Transmission electron micrograph displaying cross-sectional view of KR-E film morphology.
2. Weight gain of brominated KR-E films as function of reaction time.
3. Final KR-E film thickness as function of weight increase.
4. Relative permeabilities in brominated KR-E films reacted to 15 %W.
5. Relative permeabilities in brominated KR-E films reacted to 70 %W.
6. Separation factor vs. permeability plot for helium/methane system.
7. CO₂ permeability coefficient in brominated KR-E films as function of weight increase.
8. Scanning electron micrographs showing KR-E film cross sections at various reaction extents: a) schematic; b) 8 %W; c) 25 %W; d) 35 %W; e) 48 %W.

9. Simulated sorption curve for transient gas uptake by polymer laminate with high diffusivity skin layer.
10. Experimental sorption curve for CO₂ at 1 atm into KR-E film brominated to 25 %W.
11. Cross-sectional transmission electron micrograph of KR-E brominated to 48 %W.

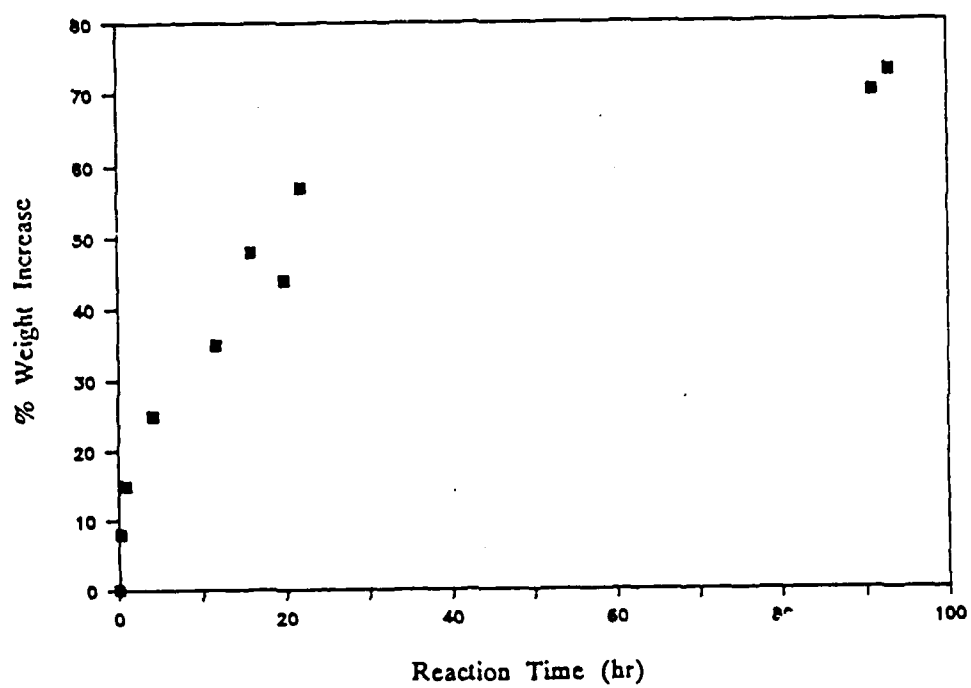
Table I
Permeability Coefficients (P) in Unmodified Films^a

	<u>He</u>	<u>Ar</u>	<u>CO₂</u>	<u>CH₄</u>
PB	47	55	435	83
PS	20	1.6	13	0.8
KR-E	21	4.2	34	6.1

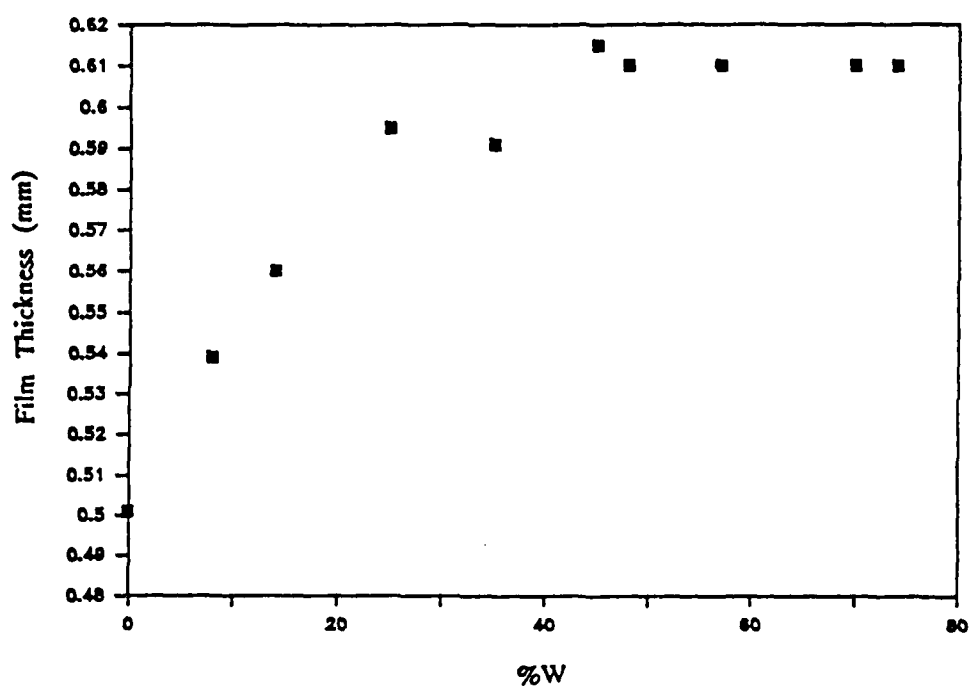
^a P in barrer = 10^{-10} cm³(STP)-cm/cm²-s-cmHg



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FIG 1

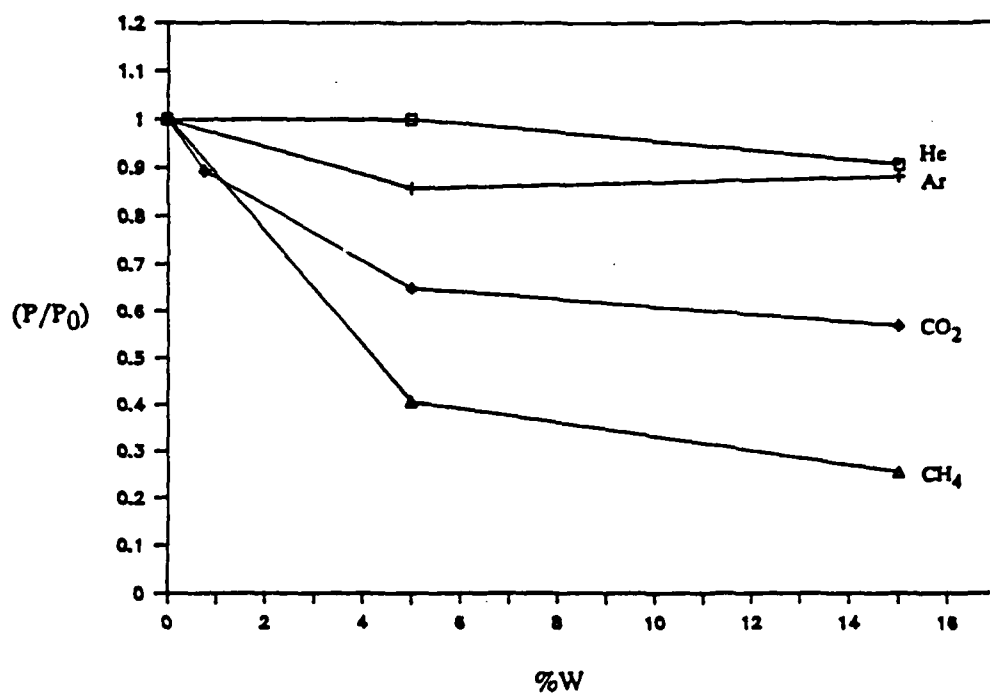


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FIG 2

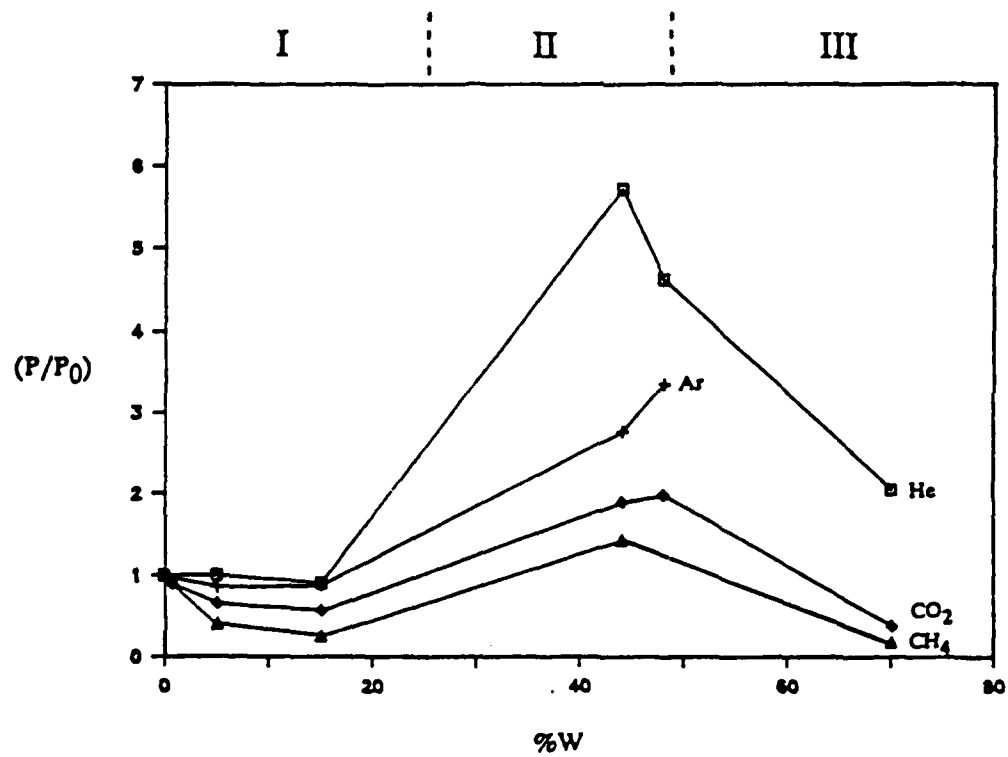


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FIG 3

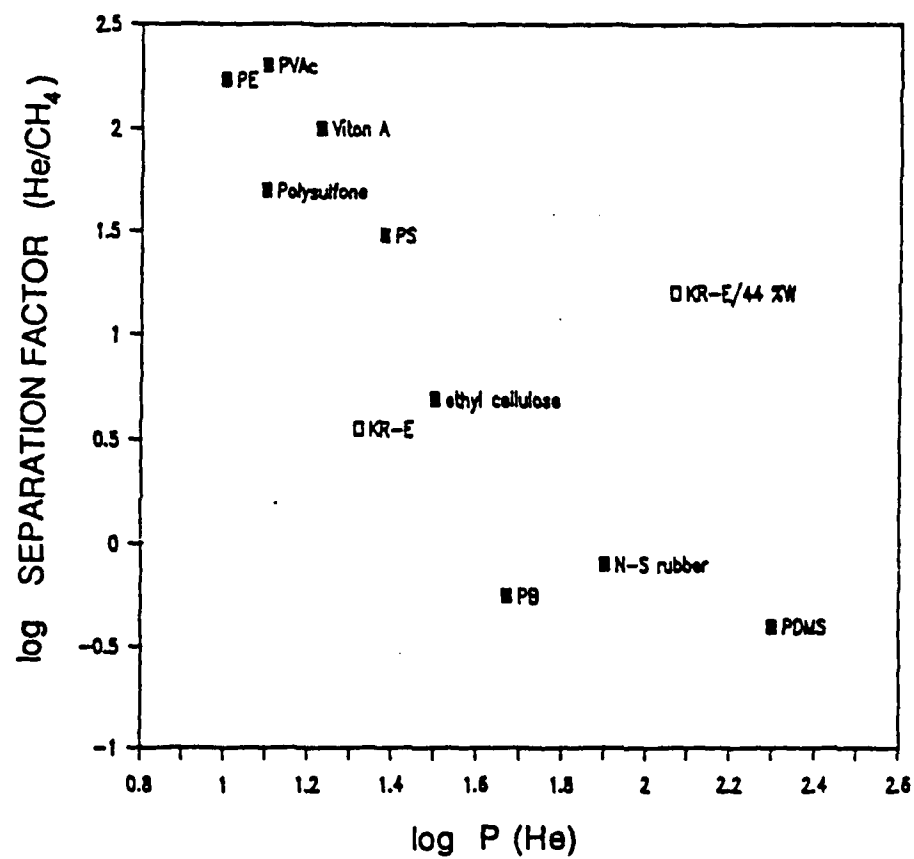


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FIG. 4



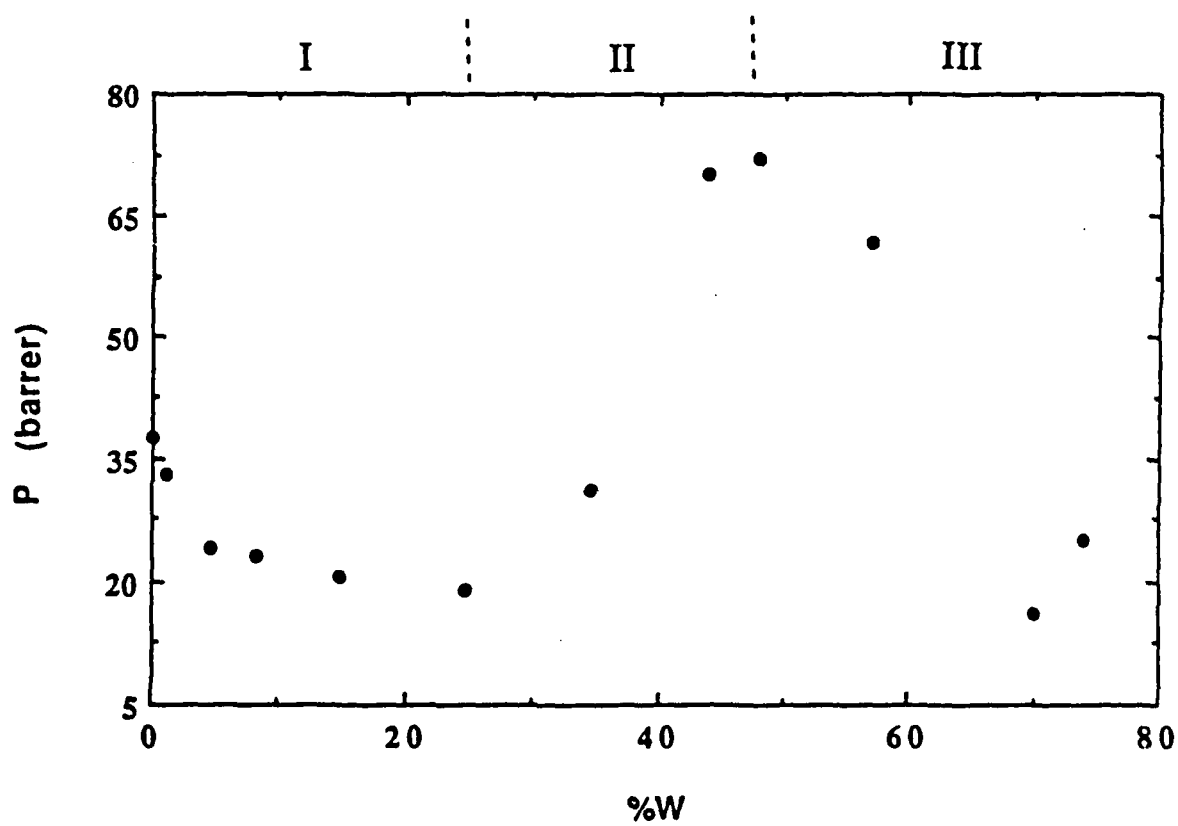
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FIG 5



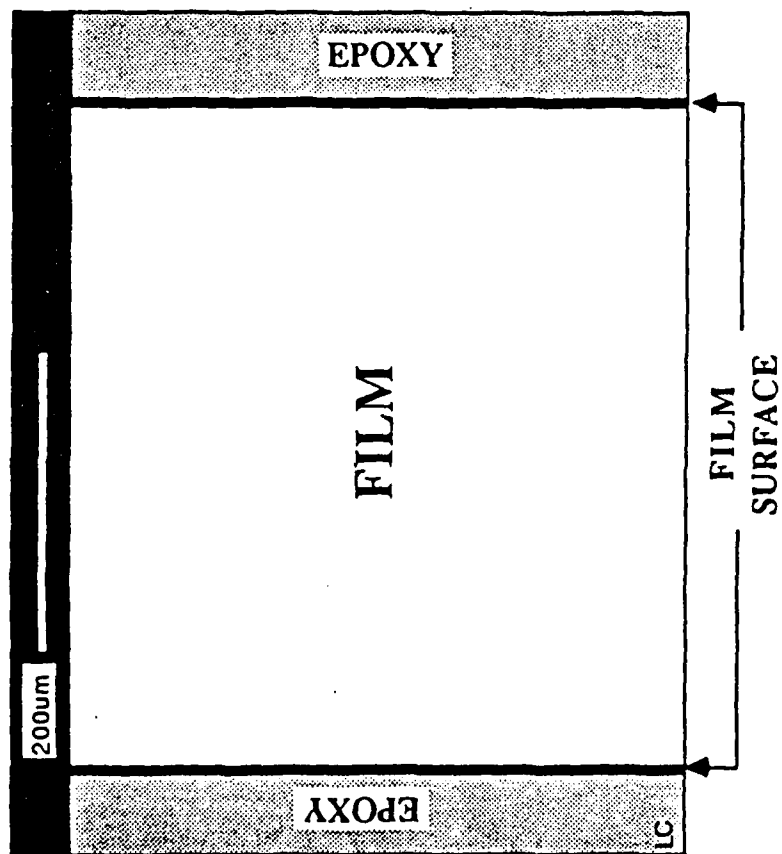
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FIG 6

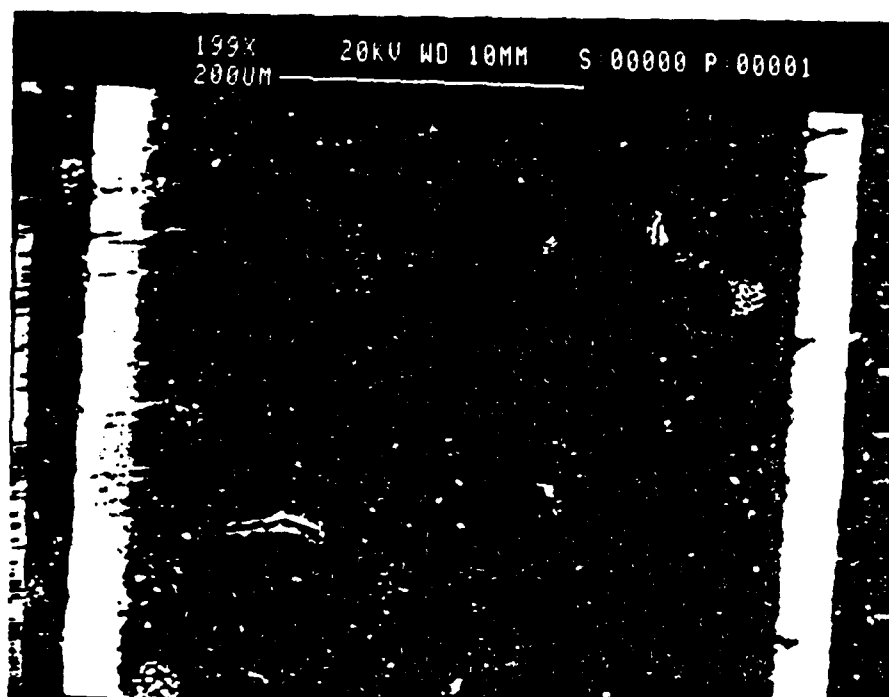


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FIG 7



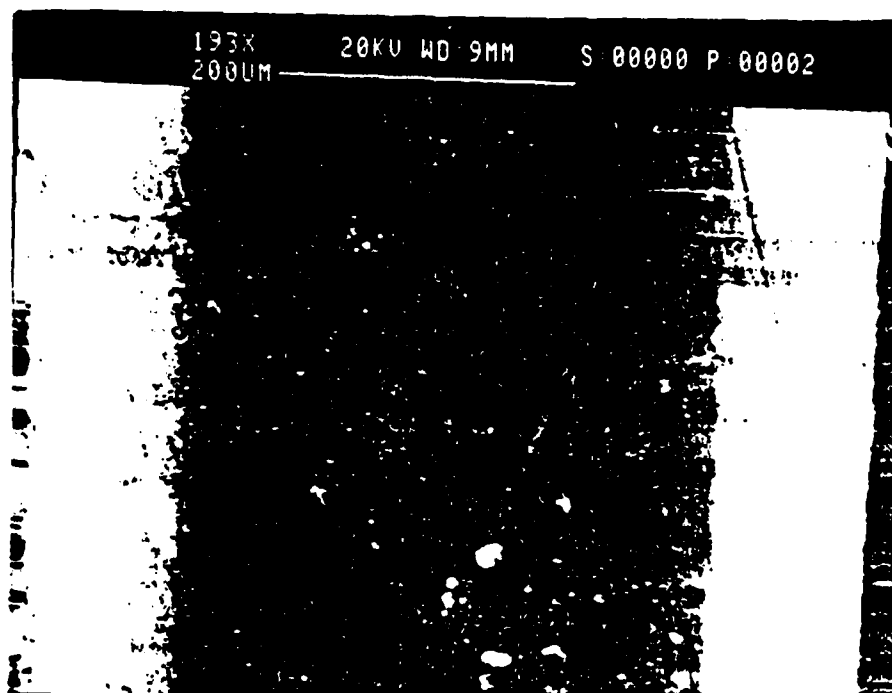
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FIG 8a



8 % W

CSEPNICA

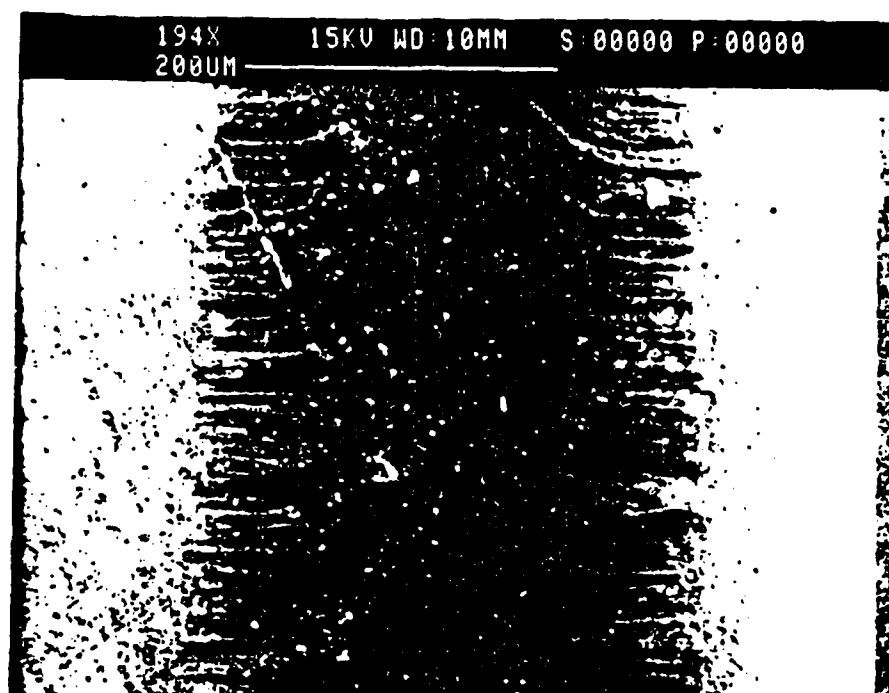
Fig 86



25 % W

CSEPNICA

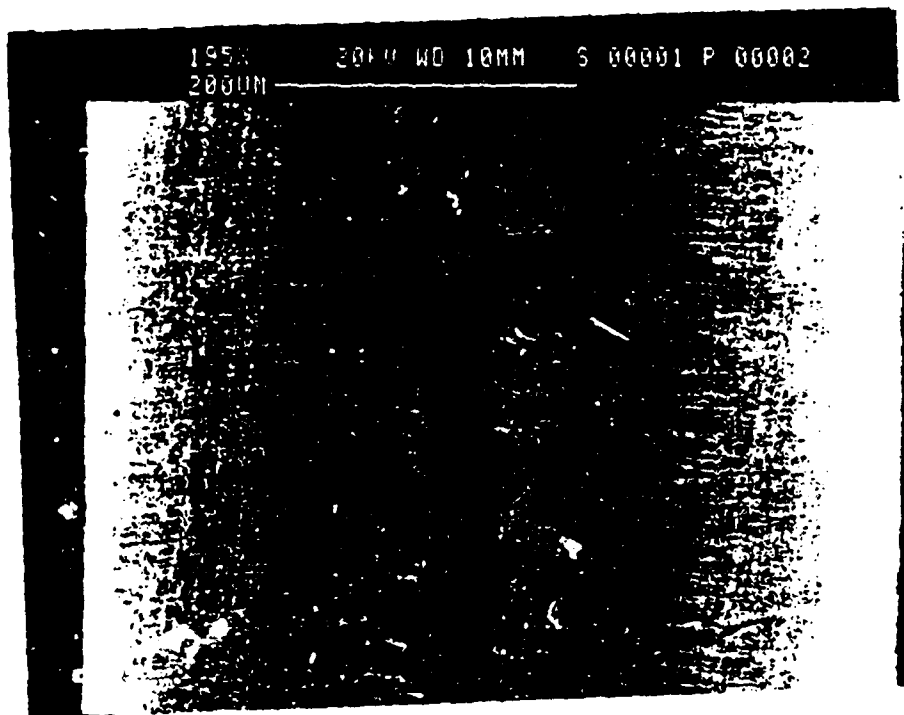
Fig 8c



35 %W

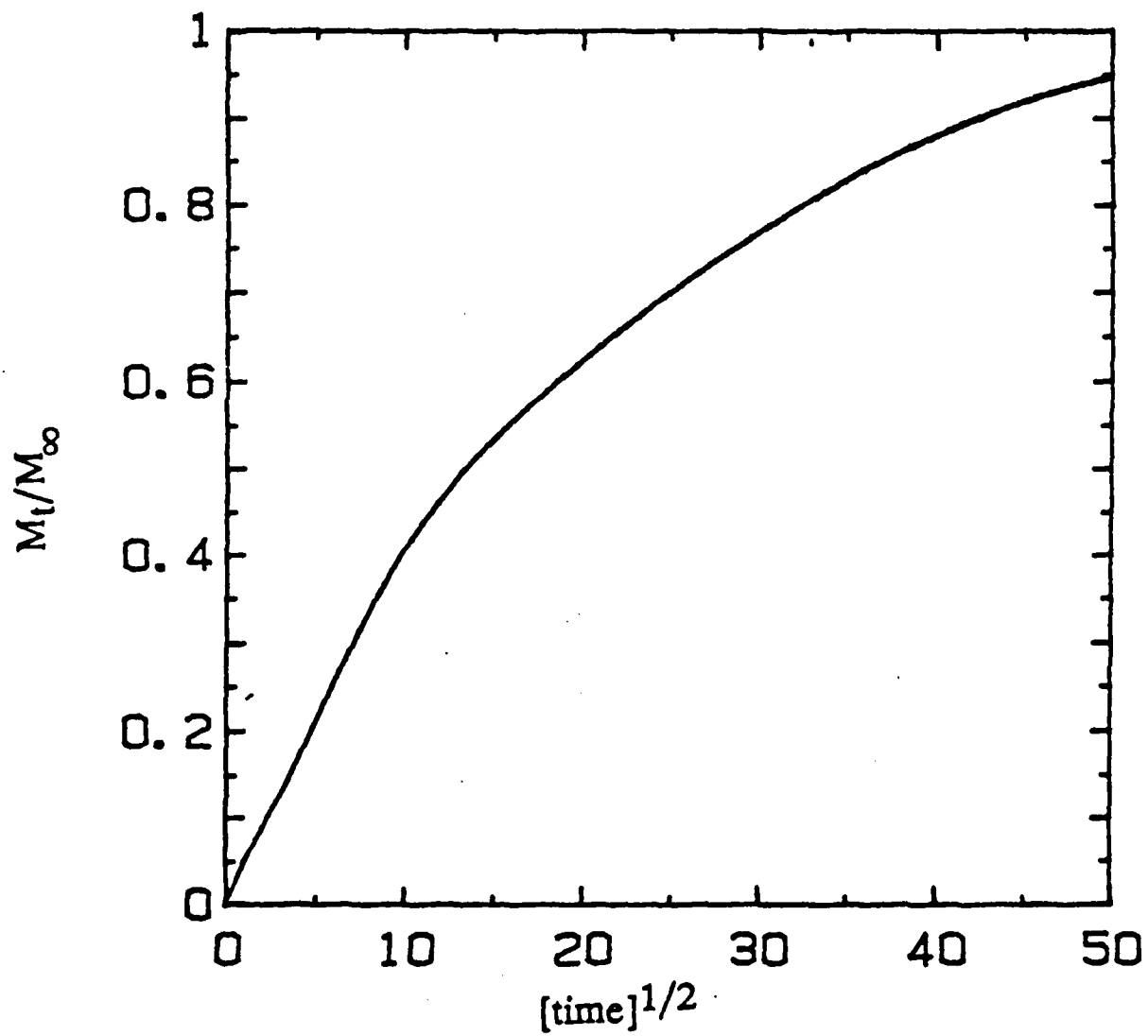
CSEPNICA

FIG 8d

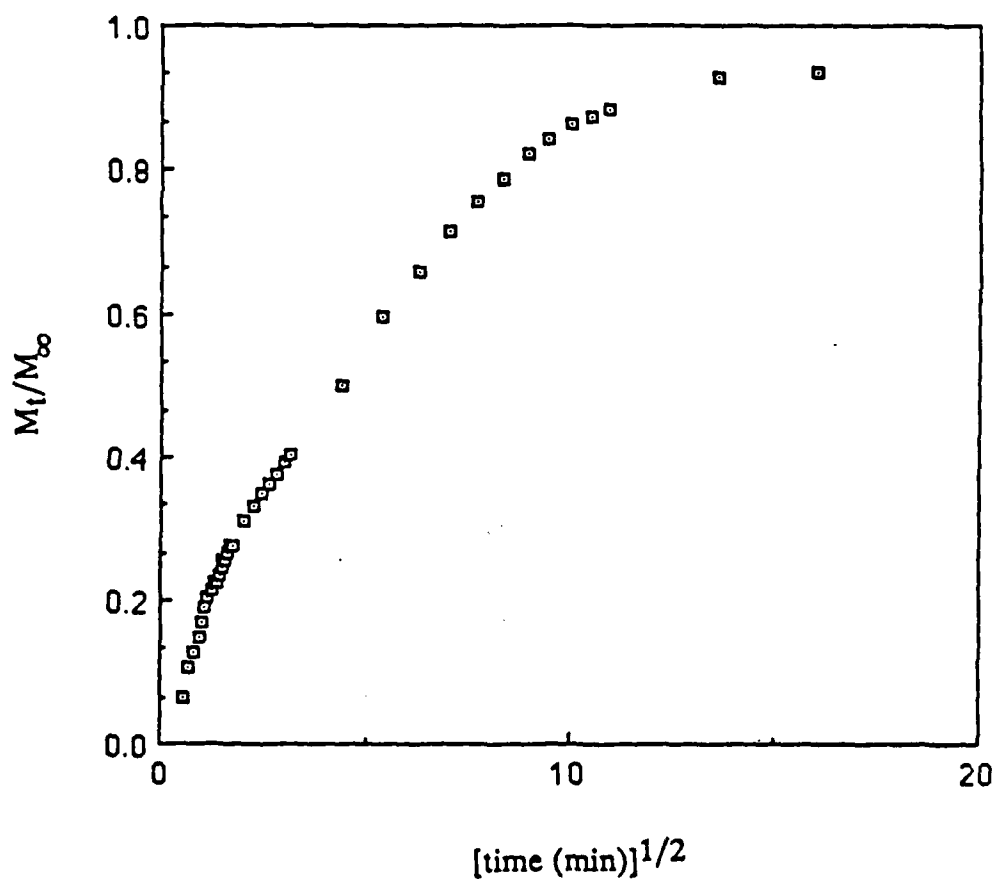


48 %W

CSERNICA
FIG 8c



CSEHNKA
FIG 9



CLEANICA

FIG 10



Cseravica
Fig. 11

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